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(54) **Ahring a halobutyl rubber**
to an unsaturated rubber

(57) The adhesion between a layer of a halobutyl rubber and a layer of an unsaturated rubber is improved by interposing a layer of a blend of a halobutyl rubber and an unsaturated rubber in a ratio of from 10 to 90 parts of the halobutyl rubber to 90 to 10 parts of the unsaturated rubber between the two layers and curing the assembly, particularly useful in bonding innerliners, treads and sidewalls to tyre carcass in the manufacture of tubeless tyres.

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SPECIFICATION

Improved adhesion of halobutyl to unsaturated rubbers

- 5 The*present invention relates to improving the adhesion of halobutyl rubbers to unsaturated rubbers. In particular the invention is concerned with improving the adhesion of halobutyl innerliners to a tyre carcass in the production of vehicle tyres. 5

A tubeless tyre generally consists of an innerliner which must be impermeable bonded to a tyre carcass which is generally a textile or steel wire web which is itself bonded to a steel belt finally covered with the tread compound. It is important that the tread has good wear resistance, good road handling characteristics and good adhesion to the carcass. Similarly it is important that the innerliner be highly impermeable and have good adhesion to the carcass. Generally the tread and tyre carcass are made from unsaturated rubbers such as polybutadiene, natural rubber, polyisopropene or the styrene/butadiene rubbers. The innerliners are generally made from a halobutyl rubber. 10 15

The tyres are made by assembling the various layers in a press where they are heated to cure the rubber and to bond the layers together.

One problem in tubeless tyre manufacture is that in using the above conventional process with a halobutyl innerliner to give improved impermeability the adhesion between the rubbers is critical. It has been suggested that the inner liner may be made of bromobutyl and this has been found to improve the adhesion. But since bromobutyl is more expensive this adds significantly to the cost of the tyre. 20

It also known to put halobutyl in tread formulations to give improved wet grip and traction but hereagain adhesion between the tread and the tyre carcass and tyre belt is of concern.

25 We have now found that satisfactory adhesion between halobutyl rubbers and unsaturated rubbers may be achieved more economically by interposing a layer of a blend of a halobutyl rubber and the unsaturated rubber between the two layers and curing the assembly. 25

The invention further provides a process for the manufacture of tyres comprising assembling a sidewall layer containing a halobutyl rubber and a tyre belt compound with a layer of a blend of from 10 parts to 90 parts by weight of a halobutyl rubber and from 90 parts to 10 parts by weight of an unsaturated rubber therebetween in a press and subjecting the assembly to a pressure and elevated temperature to bond and cure the rubber. 30

The present invention therefore provides a method of bonding halobutyl rubber containing up to 5 weight % halogen to an unsaturated rubber containing at least five units of unsaturation per 95 units of saturation by interposing a layer of a blend of from 10 parts to 90 parts of a halobutyl rubber and from 90 parts to 10 parts of an unsaturated rubber between the layers of the halobutyl and the unsaturated rubber and curing the assembly. 35

The invention further provides a process for the manufacture of tyres comprising assembling a sidewall layer containing a halobutyl rubber and a tyre belt compound with a layer of a blend of from 10 parts to 90 parts by weight of a halobutyl rubber and from 90 parts to 10 parts by weight of an unsaturated rubber therebetween in a press and subjecting the assembly to a pressure and elevated temperature to bond and cure the rubber. 40

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The invention further provides a process for the manufacture of tubeless tyres comprising assembling a halobutyl innerliner and a tyre carcass with a layer of a blend of from 10 parts to 90 parts of a halobutyl rubber and from 90 parts to 10 parts of an unsaturated rubber and a halobutyl therebetween in a press and subjecting the assembly to pressure and elevated temperature to bond and cure the rubbers. 50

55 The invention further provides a process for the manufacture of a layer of a blend of from 10 parts to 90 parts of a halobutyl rubber and from 90 parts to 10 parts of an unsaturated rubber between the tread and the carcass in a press and subjecting the assembly to pressure and elevated temperature to bond and cure the rubbers. 55

Halobutyl rubber is derived from butyl rubber. By butyl rubber we mean copolymers made from the polymerisation of reactant mixtures having 70 to 99.5 wt.% of an isoolefin having 4 to 7 carbon atoms per molecule, e.g. isobutylene and 0.5 to 30 wt.% of a conjugated multiolefin having 4 to 14 carbon atoms per molecule, e.g. isoprene, piperylene or cyclopentadiene. The resulting copolymer contains 85 to 99.8 wt.% of combined isoolefin and 0.2 to 15 wt.% of combined multiolefin. Butyl rubber generally has a viscosity average molecular weight of 20,000 to 500,000, preferably 100,000 to 600,000 and a Wijs iodine No. 0.5 to 50, preferably 1 to 15. Expressed on a molar basis the butyl rubber may have incorporated therein 60 65

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0.2 to 10 mole % of combined multiolefin, preferably 1 to 4 mole %, e.g. about 2 mole %.

Halogenated butyl rubber can be made by halogenating butyl rubber in a solution containing 1 to 60 wt.% of butyl rubber in a substantially inert C₅ to C₈ hydrocarbon solvent, such as pentane, hexane, heptane, etc. The butyl rubber cement thereby formed is halogeneated with a halogen gas, e.g. chlorine, whereby halogenated butyl rubber and a hydrogen halide are formed. Halogenated butyl rubber may also be obtained by radical halogenation of butyl rubber using an organic halogenating agent containing the NX group (where X is halogen), e.g. dichloro hydantion, dibromohydantion and chloro- or bromo succinimide.

The halogenated butyl rubber may contain up to 2 halogen atoms e.g. chlorine or bromine per double bond in the copolymer. In general halogenated butyl rubber contains at least 0.5 wt.% and preferably at least 1.0 wt.% of combined halogen. It usually has a viscosity average molecular weight of between 150,000 and 1,500,000 and a mole unsaturation of between 0.5 and 15%. A typical example of a halogenated butyl rubber is Esso chlorobutyl 10-66, a chlorinated butyl rubber containing about 1.3 wt.% chlorine having about 1.7 mole % unsaturation and a viscosity average molecular weight of about 357,000. The halogenated butyl rubber used in the blend from which the layer is made may be the same or different from that used in the interliner, bromobutyl is preferred although mixtures of halobutyls may be used.

The unsaturated rubber may be polybutadiene, polyisoprene either naturally occurring or synthetic or the well know styrene butadiene copolymer rubbers. These generally contain at least 5 units of unsaturation for 95 units of saturation. The unsaturated rubber used in the layer may be the same or different from that in the layer to be bonded, preferably it is the same.

The blend may be from 10 parts to 90 parts of the halobutyl or mixture of halobutyls and from 10 parts to 90 parts by weight of the unsaturated rubber, preferably 20 to 80 parts of the halobutyl per 80 to 20 parts of the unsaturated rubber more preferably 40 to 60 parts of the halobutyl per 60 to 40 parts of the unsaturated rubber. The thickness of the layer is unimportant but we prefer to use one as thin as possible the minimum being determined by calendering possibilities generally 0.5 mm.

In the production of tyres the layer should be interposed between the rubbers to be bonded and the bonding may be achieved during the normal finishing processes in which the various rubber compositions are cured.

Whilst the present invention is particularly suited to the production of vehicle tyres it may be used in any situation where these two types of rubber must be bonded together such as in the production of conveyor belting.

All the rubber compositions used in the present invention will generally contain the conventional curing additives, fillers, stabilisers etc.

The present invention is illustrated but in no way limited by the following examples in which Compound A was a halobutyl rubber or blends of halobutyl or blends of Halobutyl(s) with unsaturated rubbers and further containing fillers and curatives.

Compound B was made with 100 phr unsaturated rubbers, fillers and curatives.

Compound C is prepared based on a mixture of halobutyl rubbers and unsaturated rubbers, fillers and appropriate curatives.

Compound C is applied in between compounds A and B and the whole sandwich structure is then cured.

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Example 1				
Compound A was				
	Chlorobutyl	—	100	
	6PF Carbon Black	—	60	
5	Flexon 580			5
	(naphthenic oil)	—	8	
	Stearic Acid	—	1	
	ZnO	—	3	
	Sulphur	—	0.5	
10	MBTS	—	1.5	10
			(Total 174)	
Compound B was:				
	Natural rubber	—	100	
	HAF Carbon Black	—	50	
	Dutrex R	—	7	
15	Escorez 1101	—	2	15
	Stearic Acid	—	2	
	Nonox DPPD	—	1	
	ZnO	—	5	
	Sulphur	—	3	
20	MBT	—	0.25	20
	Santacuse MOR	—	0.75	
			(Total)	

Compound C is made by mixing compounds A and B in a ratio of 1/1.

- 25 Test specimens are 12.5 cm long, 2.5 cm wide were prepared from calendared layers. Each laminate has a thickness of about 1.5 mm. Insertion on one edge of the specimen of a Mylar sheet leaves the edges free for clamping in the adhesion tester. The composite pads are cured for 30 minutes at 150°C and tested for peel adhesion at room temperature and 120°C in an Instron tensometer at a 5 Cm/min jaw separation speed, with the following results

30	<i>Peel adhesion kN/m</i>			30
		Room Temperature	120°C	
35	Base Case	3.5	1.7	35
	(no layer of C present)			
	With Compound C	9.0	2.5	

- 40 **Example 2**
- Compound B of example 1 was used
- Compound A2, which is compound A of example 1 but with bromobutyl substituted for chlorobutyl was used.
- Compound C2, was a 50/50 blend of compounds A2 and B.
- 45 Using the same procedure as in example 1, the following results were obtained

	<i>Peel Adhesion kN/m</i>			
		Room Temperature	120°C	
50	Base Case	14	15	50
	With layer of Compound C2 present	36	65	

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Example 3

Compounds A and B of example 1 were used with Compound C₂ of example 2.

Using the same procedure as in examples 1 and 2 the following adhesion results were obtained.

5	<i>Peel Adhesion kN/m</i>			5
		Room Temperature	120°C	
10	Base Case (no layer of C ₂ present)	3.5	2.5	10
	With layer of Compound C ₂ present	26	50	
15				15

CLAIMS

1. A method of bonding halobutyl rubber containing up to 5 weight % halogen to an unsaturated rubber containing at least five units of unsaturation per 95 units of saturation by interposing a layer of a blend of from 10 parts to 90 parts of a halobutyl rubber and from 90 parts to 10 parts of an unsaturated rubber between the layers of the halobutyl and the unsaturated rubber and curing the assembly. 20
2. A process for the manufacture of tubeless tyres comprising assembling a halobutyl interliner and a tyre carcass with a layer of a blend of from 10 parts to 90 parts of a halobutyl rubber and from 90 parts to 10 parts of an unsaturated rubber and a halobutyl therebetween in a press and subjecting the assembly to pressure and elevated temperature to bond and cure the rubbers. 25
3. A process for the manufacture of tyres comprising assembling a tread and tyre carcass with a layer of a blend of from 10 parts to 90 parts of a halobutyl rubber and from 90 parts to 10 parts of an unsaturated rubber between the tread and the carcass in a press and subjecting the assembly to pressure and elevated temperature to bond and cure the rubbers. 30
4. A process for the manufacture of tyres comprising assembling a sidewall layer containing a halobutyl rubber and a tyre belt compound with a layer of a blend of from 10 parts to 90 parts by weight of a halobutyl rubber and from 90 parts to 10 parts by weight of an unsaturated rubber therebetween in a press and subjecting the assembly to a pressure and elevated temperature to bond and cure the rubber. 35